# CODE OF PRACTICE

# FOR

# ENVIRONMENTAL LABORATORIES

SEPTEMBER 1989



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## Table of Contents

# 1 INTRODUCTION

This paper has been prepared to guide laboratory managers and supervisors in a comprehensive review of their operating and analytical practices. It addresses the areas of staffing, laboratory facilities, analytical procedure, plus workload, records, data, and quality management. Ultimately a laboratory can consider itself credible, and accreditable, when it is able to provide an external auditor with a copy of its practices and procedures, and a copy of its own self-audit process, for review and evaluation.

This document does not describe how particular tasks must be performed, although in some cases it may indicate options. It leaves the laboratory manager free to identify and choose procedures, within the limits defined by current, generally accepted, practice. Specific operational practices and procedures must be appropriate for the company, and may well change depending on a laboratory's area of expertise, size, number of staff, equipment, source of standards and supplies, level of computerization, etcetera.

Management is accountable to the laboratory client to demonstrate how the goal of continued, adequate, well-documented data quality is achieved. Ultimately, a good quality management program will enhance a laboratory's ability to perform analytical tests with the desired reliability. Adherence to this code will indicate the laboratory's readiness to monitor and control quality.

## 1.1 Background

Environmental studies require extensive planning to ensure that samples taken are representative of the environment being observed, and that all sampling procedures, sample handling and preservation, and analytical procedures used will be of sufficient quality to ensure that project data quality objectives are met.

Laboratories must be able to provide evidence that the quality of their data will meet the specific data quality objectives of a client's project. Quality is achieved and maintained by using well established practices to ascertain and assure that systems and supplies are under control. The absence of documentation leaves room for tasks to be changed or forgotten as staff rotate through the working groups or leave the company. Therefore this paper identifies the types of factors that should be documented.

The selection of a laboratory is a critical component in project planning. While it is assumed that laboratories are generally operated in a professional and competent fashion, ability to obtain a contract often depends on rumours about previous performance, good or bad. The increasing cost of analytical services creates a very competitive environment within which the development of proper quality management practices does not always receive the attention it deserves. And yet the documentation of these practices is exactly what the client would like to review.

All laboratories must strive to provide timely, professional, and accurate service in their specific areas of competence. A 'minimum standard' for specific practices is difficult to determine in a generic sense, since it will depend on project needs. Therefore, when contracting for analytical services, both the laboratory client and the laboratory management must ensure that the 'minimum standard' is clarified and written into the contract as appropriate. This will usually include specification of the methods to be used and the performance level to be achieved.

The key to reliability is documentation. In particular, the thorough documentation of policies and procedures is a critical component of a laboratory's operational review. All aspects of laboratory management and operation must be considered. Section 2 provides a management overview of the topics discussed in more detail in subsequent sections.

But, documentation does not itself ensure that staff will implement the practices described, or that the desired level of data quality will be achieved. A proper quality management system will provide evidence that predetermined procedures and practices were established and implemented, that the quality of service provided is continually evaluated, controlled and recorded, and that the quality of data generated does meet the client's data quality requirements. The area of laboratory quality management is addressed in Section 3.

## 1.2 Overview of Terminology

There have been important advances in the understanding and implementation of control and data quality management in the analytical laboratory environment over the past decade. The interpretation and usage of quality assurance and performance management terminology depends somewhat on which international standards association one is associated with, and the interval since their definition was formally adopted. Thus the ASTM Compilation of Standard Definitions (1982) provides several definitions for accuracy (closeness to target), each of which depends on the context of use. None of these definitions incorporate the need to demonstrate and maintain control. Surely accuracy should depend on technique, skill and control, not just luck.

Analytical measurement systems include the need for an accurate standard, a stable, properly calibrated, analyte detection and quantitation process, a specific set of criteria which identify the analyte(s) that may respond to the test conditions, and an efficient, rugged, sample preparation procedure that effectively eliminates interference from the sample matrix. Much of the terminology of quality management derives from industrial process control where these non-quantitative aspects of chemical or bio-chemical measurement systems are not encountered.

The terms used in this text are defined at the beginning of the relevant sections. The more significant terms are identified below.

Management Terms

The development and implementation of a proper quality management program depends on documented policies, guidelines, protocols, and procedures. (See section 2 for definitions.)

Quality Management Terms

The management of analytical quality requires an understanding of the concepts of data quality, quality planning, quality assurance, and quality control. (See section 2 for definitions.)

Method Practices Terms

The production of good quality analytical laboratory data requires use of analytical procedures based on standard methods and standard operating practices. Staff must be properly trained in these and related good laboratory practices.

Method Performance Terms

The proper application of a method to a particular sample matrix may require careful testing to verify its suitability. Factors to be evaluated include; repeatability, ruggedness, sensitivity, specificity, and recovery. (See section 8).

Precision, Accuracy, and Control Terms

Analytical precision and accuracy reflect the training and skill of the laboratory specialist in the day-to-day use and calibration of analytical methods and equipment. The attainment of precision and accuracy requires deliberate control over the quality of calibration standards and techniques. (See section 9).

The concept of control requires a clear distinction between acceptable variation (deviation) and unacceptable variation (error). Measurements are expected to vary within a range based on the method's repeatability, and within this range replicate measurements should be essentially normally distributed. Outliers from this range are indicative of error.

The application of statistical quality control assigns control and warning limits relative to the expected value of a control sample. These limits are based on the analytical repeatability (single analyst, within-batch replication). Any point falling outside this range (an outlier) represents an error which requires investigation. Errors result from indeterminate, determinate, systematic causes. Systematic errors arise from inadequate control of calibration processes.

Any undetected trends which cause the average of a sequence of results to drift away from the expected value are indicative of bias. Bias is often induced by systematic error in calibration. It may also result from methods based on distinctly different principles due to their effect on method recovery or analytical response.

# 2 LABORATORY MANAGEMENT RESPONSIBILITIES

It is the responsibility of management to implement a process which will establish, demonstrate, and maintain the quality of all laboratory operations. This section reviews the factors critical to a well-controlled analytical laboratory. Section 3 outlines the components of a quality management program.

Attainment and documentation of quality is ultimately linked to development and implementation of documented control processes. These processes require planning, top management involvement to define goals and ensure resources, middle management involvement to define needs and procedures, and total commitment of all personnel to ensure implementation and proper response.

## 2.1 Definitions

### 2.1.1 Guidelines

Descriptions of general principles to be followed in developing operational protocols and procedures, including the selection of appropriate alternatives.

### 2.1.2 Policy

Description of activities considered by management as essential to proper operation, often prefaced by a statement such as "Staff must ensure that ...".

### 2.1.3 Protocols

Descriptions of the approach to be taken in implementing and reporting the completion of day-to-day operations, including what is to be done, who is responsible, and forms to be used. For example; sample submission, data reporting, workload management.

### 2.1.4 Procedures

Descriptions, step by step, of the operations to be performed to accomplish a specific task. They provide the basis for staff training and subsequent audits, for example; analytical methods, safety procedures, computer sign-on and data entry procedures.

### 2.1.5 Data Quality

The suitability of data for its intended use.

Documented evidence of the reliability of data in terms of factors such as; analytical precision and accuracy, recovery, specificity and identification, and freedom from sources of bias or error which can occur at any stage in the sampling and analytical process.

### 2.1.6 Quality Management

Activities undertaken by management to ensure the development, implementation, and verification of a product quality program, by assignment of responsibilities, and by resource management.

### 2.1.7 Quality Planning

Activities undertaken to ensure that the equipment and services available will provide the level of quality required to meet predetermined data quality objectives.

### 2.1.8 Quality Assurance

Activities undertaken by line supervisors, and designated QA personnel; to identify critical operations that may adversely affect the quality of product; to establish appropriate control procedures; and to ensure that product quality is evaluated and documented.

### 2.1.9 Quality Control

Activities undertaken by staff in accordance with established QA requirements to verify total system readiness for use.

## 2.2 Committment to Quality

The Quality Assurance program, including all aspects of quality management, quality assurance, and quality control, must be documented and must meet the minimum standards outlined in subsequent sections of this document. Details are provided in section 3.

The planning and formulation of organizational policies must ensure in particular that:

- o positions associated with work for a specific analytical services project are identified;
- o all affected staff are aware of their responsibilities;
- o effective channels of communication are established to ensure efficient transfer of information;
- o all policies, guidelines, protocols, and procedures are documented and known to staff;
- o staff receive ongoing technical and other training appropriate to their current or future responsibilities.

## 2.3 Documentation

All company policies, guidelines, protocols, and procedures must be documented so that staff may know their specific duties and responsibilities with respect to good laboratory practice and standard operating practices.

Protocols for reviewing, updating, approving, and distributing revisions to current documentation must be established.

Data quality derives from the careful review and evaluation of all aspects of day-to-day activity. Proper documentation will permit identification of control problems and the implementation of control procedures. The following factors are discussed in more detail in later sections.

Areas to be considered for documentation include:

- o Laboratory Management (systems and operations)
- o Analytical Methods (techniques, apparatus, procedures)
- o Sample Management (sample log-in and throughput)
- o Test Result Management (records, evaluation, reporting)
- o QC Data Management (archiving and retrieval)
- o Quality Evaluation (systems, procedures, performance)
- o Document Review and Revision.

## 2.4 Organization

A laboratory wishing to provide analytical service must detail its organizational structure and human resources, as they relate to the service to be provided. This documentation must address the services provided, and the qualifications of staff. Details are provided in section 4.

Services

The general objectives of the organization with respect to services provided must be specified, including a listing of those services available in-house and those available by sub-contract.

Staff Qualifications

The minimum qualifications, skills, and experience required of staff performing analytical tests must be documented. The actual skills and experience of staff should be evaluated and documented.

The need for a formal skills evaluation process for specific tasks, operations, or tests should be assessed, and implemented where necessary.

## 2.5 Facilities

The physical facilities available for receiving, storing, handling, and analysing samples must be documented and must meet a minimum standard appropriate to the service being provided. Details are provided in section 5.

## 2.6 Sample/Workload Management

The procedures employed for sample management throughout the laboratory must be documented. These will include:

- o Sample reception and log-in;
- o Test and work assignment;
- o Sample storage, preservation;
- o Sample chain of custody;
- o Analytical throughput;
- o Report preparation and review.

Adequate space and staffing must be provided to ensure speedy reception of samples, correct test assignment, timely initiation of analysis, and timely and accurate reporting of analytical results. Adequate space must be provided to ensure and maintain the integrity of samples. Details are provided in section 6.

## 2.7 Analytical Systems

Analytical equipment, and instrumentation must be appropriate to meet the specified quality requirements of the laboratory's clients. All equipment and instrumentation must be kept in good repair and must be suitable for the task. Equipment and instrumentation must be checked regularly to ensure physical calibration (e.g. length, temperature, weight, alignment) is maintained. The response of analytical detection systems must be calibrated regularly against solutions of known concentration.

Reagents, solvents, standards, glassware and other laboratory supplies must be stored safely and in appropriate locations. They must be ensured suitable for use. Quality requirements must be documented and known to those responsible for providing laboratory supplies and services. Details are provided in section 7.

## 2.8 Methodology/Procedures

The methods and analytical practices employed must be fully documented. The expected performance characteristics of these systems must be determined and available for scrutiny. Use of a 'Standard Method' promotes comparability of data among laboratories. Deviations from the use of a standard method must be thoroughly documented. Details are discussed in section 8.

## 2.9 Analytical Control

Analytical systems must be controlled. The characteristics include calibration accuracy and reproducibility, method recovery, and analytical repeatability. Performance control limits must be established. These should be based on the within-batch repeatability of analysis for typical samples in the desired operating range. Excessive between-run variability indicates lack of precision control. A trend over time indicates lack of accuracy control.

Control charting is highly recommended to maintain both reproducibility and accuracy. Regular use of fresh reference standards for bias control, and appropriate certified reference materials for recovery control, plus regular participation in interlaboratory comparability studies, are all important aspects of a comprehensive analytical performance control program. More details are provided in section 9.

## 2.10 Data Reporting

Data reporting practices must be defined to ensure results are recorded to sufficient significant figures, and that test names, methods, and units of measure, and all important data quality and related qualifiers are recorded and reported. Any policy regarding the reporting or with-holding of low-level data should recognize the danger of both false positive and false negative decision errors on the part of the data user. See section 10.

## 2.11 Records Management

Formal data recording and reporting practices must be established to ensure that the quality of a reported result is known and that it is traceable back to the raw information on which it is based. A formal policy must be established to ensure secure retention of laboratory records. Details are provided in section 11.

# 3 QUALITY MANAGEMENT

Laboratories wishing to ensure good quality analytical services must develop and establish a comprehensive Quality Management program to document and define the tasks and responsibilities of all staff associated with the analysis of samples. The goal of such a program is to establish and maintain operational and data quality at all levels of operation.

## 3.1 QM Program Documentation

One or more documents must be available which address the following areas:

- o Quality Management (staff roles and responsibilities);
- o Data Quality Objectives (client data quality needs);
- o Quality Assurance (identification, assessment, correction, monitoring of sources of quality degradation);
- o Quality Control (protocols for monitoring the quality of supplies, equipment, method and analyst performance).
- o Audits (system verification)

## 3.2 Quality Management Plan

There must be a current document outlining the company's Quality Management strategy. The objective of this plan is to ensure measurement data of known and acceptable quality. This plan shall:

- o delegate responsibility for the various activities that comprise the quality program;
- o define the mechanisms established to assure completeness and integration of all components of the program; and
- o define reporting channels for professional and other departmental QA activities.

### 3.2.1 Staff QM Responsibilities

The Quality Management Plan shall describe the roles and responsibilities of management, supervisors and the Quality Assurance Officer.

Typical Quality Management activities will include:

- o identifying staff roles and responsibilities;
- o establishing laboratory policy, guidelines;
- o establishing operational protocols, procedures;
- o verifying implementation of all QM/QA/QC activities;
- o auditing system procedure and performance and verifying control status;
- o ensuring QA/QC information is acted on, and reporting frequency and impact of control failures and actions taken;
- o other related activities.

## 3.3 Data Quality Objectives

There must be a current document which describes the data quality objectives of the laboratory client and the process whereby they will be met. A specific person should be responsible for establishing this Data Quality plan.

### 3.3.1 Data Quality Planning

Typical data quality planning needs include:

- o definition of project objectives;
- o definition of data needs;
- o definition of data quality needs;
- o selection of parameters to be measured;
- o planning of field activities where needed;
- o selection of field procedures;
- o selection of analytical methods;
- o definition and planning of project QC;
- o documentation and audits of project quality;
- o definition and documentation of limitations;
- o other related planning activities.

## 3.4 Quality Assurance Manual

There must be a current document outlining the Data Quality Assurance program. This document shall cover the areas of quality assurance and assessment, and the mechanisms established for problem detection and correction.

### 3.4.1 Supervisory QA Tasks

The Quality Assurance manual should identify and describe the routine activities of supervisory personnel with respect to quality assurance.

Typical supervisory QA activities will include:

- o documentation and supervision of methods;
- o identification of critical steps in the method;
- o definition of control activities and frequency;
- o definition of control protocols;
- o monitoring performance;
- o follow-up on problems identified;
- o between method comparisons;
- o between laboratory comparisons;
- o other related activities.

### 3.4.2 System Performance Assessment

The Quality Assurance manual should address the protocols available for assessing the performance of all significant components within the test measurement process. Typical system QA will monitor:

- o the analyst (skilled, experienced);
- o laboratory facilities (clean, well-equipped);
- o the sample (valid, representative);
- o sample preparation and the analytical process (rugged, appropriate and well-documented);
- o the measurement system (sensitive, stable, and properly calibrated);
- o data reporting (properly evaluated and qualified);
- o data interpretation (valid controlled);
- o data management (secure, accurate).

## 3.5 Quality Control Manual

There must be a current document outlining the laboratory's Quality Control activities and protocols. This document shall cover the areas of pre-service and in-service QC checks, run control and data quality documentation.

### 3.5.1 Pre-service QC

The Quality Control manual will include a description of the activities required of the individual analyst to monitor and ensure the suitability of laboratory reagents, supplies, equipment, instrumentation, etc., prior to use.

Typical pre-service QC activities will address:

- o cleanliness of labwares, reagent purity;
- o equipment operation, instrument stability;
- o instrument detector conditions, drift, noise, response factors, retention times, etc.;
- o calibration zero, slope, curvature, day-to-day stability;
- o background noise, matrix effects; and
- o other supply-related quality concerns.

### 3.5.2 In-Service QC

The Quality Control manual will include a description of the in-service quality checks performed to monitor the performance of the method, the instrumentation, and the analyst during analysis and measurement. These may include checks on field activities and sample quality.

Typical checks on in-service quality include:

- o reagent (method) blanks;
- o instrument sensitivity and response stability checks;
- o equipment maintenance checks;
- o spot checks on staff technique, staff retraining;
- o inter-method, inter-lab, inter-analyst checks.

Typical checks on sample quality include:

- o container quality checks (travelling blanks);
- o field equipment evaluations;
- o field instrumentation checks;
- o sampling procedure (field spikes, duplicates);
- o spot checks on staff technique, staff training.

### 3.5.3 QC Records

The Quality Control manual will include examples of QC record formats, control charting, discussion of actions to be taken, and regular sign-off by supervisory and quality assurance personnel.

Time sequence charts of information such as instrument response, incubator temperature, can be drawn to show an expected value and action limits. They provide a visual record of operating conditions, and are of use for monitoring trends and for initiating equipment maintenance activity.

### 3.5.4 Run Quality Documentation

The Quality Control manual will describe the activities and procedures followed to evaluate and maintain the control status of an analytical run, and the action to be taken when problems are identified.

Typical documentation of an analytical run will include the results obtained for:

- o method blanks;
- o calibration control standards;
- o method control samples (in-house);
- o reference standards (accuracy checks);
- o reference materials (method recovery checks);
- o duplicate analysis;
- o recovery of method 'spikes'
  (matrix effects, digestion or extraction efficiency);
- o recovery of pre-injection 'spikes'
  (internal standards, surrogates, etc.);

plus other checks as needed for specific instrumentation, sample matrices or steps within the analytical method.

### 3.5.5 Performance Documentation

The Quality Control manual must specify procedures used to summarize and report performance. Control charting is strongly recommended for those systems subject to chronic systematic variation.

Typical run performance reports will address:

- o repeatability (within-run duplicates);
- o reproducibility (between-run, between-analyst control);
- o method ruggedness, recovery;
- o instrument control (stability, sensitivity, response, linearity);
- o accuracy of standards and calibration;
- o blank correction estimation and control;
- o matrix effects, interferences, etc.

## 3.6 Audit Manual

A QA Audit manual should be available which describes the mechanism for independent verification that all required QA/QC activities are implemented, and that the quality of data meets the required standard. Audits should evaluate the accuracy and traceability of standards, the documentation, proper implementation, and controlled performance of analytical procedures, the data quality documentation, quality of materials, maintenance of equipment, the routine laboratory operational practices, and the overall quality management system.

### 3.6.1 Audit Activities

Audits may include activities such as:

- o inter-laboratory comparisons;
- o submission of check standards/samples;
- o internal blind checks prepared and distributed by an independent source within the company;
- o inspection of analytical and related procedures;
- o inspection of QA/QC records and related maintenance log-books, etc., including control status evaluation;
- o evaluation of operating practices
- o evaluation of the quality management system.

## 3.7 Control Charting

Control charts are primarily used to evaluate the end result of a process although they also have use in ensuring the continued quality of critical components. Control charting is strongly recommended for those systems subject to chronic systematic variation. The major source of between-run, (systematic) error is the re-standardization or calibration step which assigns correction factors for the intercept and slope of the response vs concentration or weight curve.

Although most appreciate the use control charts for detecting outliers, there is less awareness of their use in detecting and preventing trends. Trends are often induced by inadequate attention to ensure accurate calibration of analytical instrumentation.

The estimates of the average and standard deviation for a specific set of data are independent of the order in which the data occurs. But, if the data happens to be ordered in sequence from lowest to highest, one would recognize a trend, which would suggest the analytical system is drifting significantly. Such drift must be prevented. This is assured by establishing between-run control and warning limits defined by the within-run estimate of repeatability ($S_w$). The principles and procedures of control charting are described in a number of the texts in section 12.

### 3.7.1 MOE Control Practices

The following is an overview of the various control procedures used in Ontario Ministry of the Environment (MOE) labs. For more detailed information refer to the reading list. The control procedures include;

Shewhart control charting,
Two-Sample control charting, and
Single sample control.

In general, where slope control is a particular problem, or the blank is known to be an insignificant source of day-to-day variation, the Shewhart control procedure based on duplicate analysis of a single control sample is acceptable. This technique is described in detail in texts on statistical quality control.

When the slope is reasonably well controlled, the Two Sample option is preferred since it distinguishes between slope and blank related sources of systematic error. This procedure, developed by King, based on the two-sample Youden procedure for interlaboratory comparison , has been in use in MOE labs since 1972.

The Single Sample option is the least acceptable option, because it does not readily distinguish between random and systematic sources of calibration variation/error.

### 3.7.2 Shewhart Control: Average and Range Charts

A single sample is set aside as a 'control'. It is analysed in duplicate once per batch to yield results $X_1$ and $X_2$. These values are used to calculate a range (R) and an average ($X_{avg}$). The average range ($R_{avg}$) over a period of time is used to estimate within-batch repeatability ($R_{avg} = 1.128\ S_w$) and to set control limits for the range and average.

This procedure detects between-run systematic error in the average result, by applying control limits based on the repeatability. The control limit for the average is set at 1.88 $R_{avg}$ or 2.12 $S_w$. Since the confidence interval for the average is 1.414 times tighter than for a single value, this approach is equivalent to but more powerful than a 3 S limit on a single result. Warning limits are set at 2/3 of the control limit.

Systematic error can be introduced by either slope or blank correction bias. This technique responds indiscriminately to both. Users must avoid the tendency to 'correct' the slope without checking first for a possible error in the blank or background correction. Otherwise the proper corrective action may not be taken.

### 3.7.3 Two-Sample Control: Sum-Difference Charts

Two control samples (A and B) are selected to cover the bottom and top end of the operating scale, for example, at 25% and 75% of full scale. Each sample is analysed once per run. The individual results, and their sums and differences are recorded.

The standard deviations ($S_a$ and $S_b$) for these two control samples can be calculated over a period of time, and compared. If the ratio exceeds about two then inadequate control of slope may often be the cause.

The difference between the two control results is a direct measure of slope. If the differences are reasonably stable and less variable than the sums, systematic error in the sum can be directly attributed to faulty blank or background correction.

As long as the slope is in reasonable control, the standard deviation of the differences ($S_d$) is an estimate of within-batch variability, and is approximately 1.414 larger than $S_w$. Control limits for differences are set at $\pm 3\ S_d$. Warning limits are set at $\pm 2\ S_d$.

The standard deviation of the sums ($S_s$) is a measure of between-batch variability (S). If the ratio of $S_s / S_d$ exceeds 1.3 to 1.5, then poor control of systematic error can be inferred. To forestall this, the control limit for the sums is set at $\pm 4\ S_d$. Warning limits are set at $\pm 2\ S_d$.

### 3.7.4 Single Sample Control

A single control sample is analysed only once per batch. This approach is much less powerful in detecting bias than the previous two procedures. The standard deviation of the accumulated control data is a between-batch estimate. Obviously, in as much as the process is not already under statistical control (i.e. there are trends in the data over time), the control limits will be too wide. The control limits for such data must not be calculated from the data itself because of the strong likelihood that the process is not adequately controlled.

An independent estimate of within-batch variability ($S_w$) is required in order to set proper control limits. Control limits should be set at 4 $S_w$. Warning limits are set at 2 $S_w$. If a result is found to be out of control, other QC data is required in order to assign a cause.

One mechanism for evaluating the possibility of systematic error in data from a single control sample follows.

Adjacent results can be paired (as duplicates) and used to calculate a standard deviation. If this estimate is less than 2/3 of the estimate obtained using all the data, one can conclude that the data includes a significant component of drift (i.e. is not randomly distributed over time), and is probably out of statistical control.

### 3.7.5 Estimating Standard Deviation

Method repeatability is estimated by calculating the standard deviation of a series of replicated measurements representing within-batch, skilled analyst performance. Under controlled conditions (i.e. within a single batch of trials), a well documented and proven method is expected to provide a certain level of repeatability.

Note however, that the observed estimate (S) can deviate from the actual value ($\sigma$) by as much as 50% depending on the amount of data collected. And the population value is expected to change slightly from day to day and from analyst to analyst depending on skill and materials available.

The replicate analyses should be performed within the same batch, since between-batch analyses include the effect of day-to-day calibration biases. The measurement of replicate analyses should be spaced throughout the run (i.e. not sequentially).

The within-batch standard deviation $S_w$ can be estimated by;

a) multiple replicate analysis of a single sample,
b) duplicate analysis of several samples,
c) estimate based on the average range for a set of duplicates.

For case a):

$$S_w^2 = \frac{n.\ \Sigma (x_i^2) - (\Sigma x_i)^2}{n.\ (n-1)}$$

where $x_i$ = ith of n replicates

For case b):

$$S_w^2 = \frac{\Sigma (D_i^2)}{2.\ k}$$

where $D_i$ = difference between ith pair of k duplicate pairs

note: individual duplicate pairs can be taken from different batches.

For case c):

$S_w$ can also be **estimated** from the average difference ('range') between the duplicate pairs in case b).

$$S_w = 0.8865\ (\Sigma D) / k$$

While it is easier to calculate by hand, for a given set of data these two estimates will probably not be equal. This approach is less sensitive to the effect of inadvertently including within the data set duplicate pairs with unexpectedly large differences.

In general, any data indicative of a possible control problem should be excluded when estimating precision for the purposes of setting control limits.

# 4 ORGANIZATION

The organizational structure with respect to analytical services must be documented in terms of:

- o the management structure;
- o the relationship of laboratory services to other company operations;
- o relationship to sub-contracted operations;
- o the staffing structure with respect to analytical services;
- o reporting relationships and lines of communication;
- o a current plan describing the positions and responsibilities.

## 4.1 Services

There must be a current document describing the services available and the way in which the company is structured to provide them. This document will affirm the goal to ensure data of known and acceptable quality.

## 4.2 Staffing

The organizational structure of a laboratory providing analyses must designate the positions responsible for ensuring general compliance with this code. These positions should include as appropriate;

- o company management,
- o laboratory director,
- o quality assurance officer,
- o supervisory personnel,
- o scientific personnel,
- o technical personnel,
- o secretarial and clerical personnel,
- o related operations and support services personnel.

### 4.2.1 Laboratory Director

The laboratory director(s) must be sufficiently qualified to assume professional, organizational, and administrative responsibility for the facilities and for the quality of services rendered.

### 4.2.2 Quality Assurance

There must be a position specifically responsible for developing, implementing, and auditting the Quality Assurance program and verifying the production of records to document the quality achieved.

### 4.2.3 Supervisors

There must be a position or positions specifically responsible for the routine technical and professional operation of the laboratory facilities and the analytical services rendered. These positions must be responsible for timely production of results of known and acceptable quality, as per client specifications.

### 4.2.4 Support Staff

There must be sufficient scientific, technical, and clerical positions to provide for:

- o supervision of analytical testing and data quality;
- o all specified requirements for workload management and throughput;
- o timely reporting of test results to meet client needs

## 4.3 Staff Qualifications & Training

All scientific and technical personnel must have appropriate training and experience which suits them for their professional responsibilities. These qualifications, on either an individual or class basis, should be available for scrutiny as appropriate.

### 4.3.1 In-service Training

Management must provide in-service orientation and training in job-related duties such as safety, quality control and quality assurance, analytical procedure, standard operating practices.

### 4.3.2 Training Records

Records of on-job or off-job, formal and informal training, should be retained to assist in scheduling retests and refresher courses.

### 4.3.3 Proficiency

Staff involved in providing analytical testing services must be familiar with and proficient in the procedures involved, and qualified to meet the appropriate requirements of this code. The mechanisms for evaluating proficiency must be documented.

### 4.3.4 Continuing Education

Management should emphasize and provide for continuing education programs for all staff involved in laboratory services to ensure their skills and knowledge reflect current advances in their field.

Staff should be encouraged to attend meetings or seminars relevant to the requirements of their profession.

# 5 PHYSICAL FACILITIES AND SERVICES

The laboratory areas and associated facilities must provide space sufficient to perform the tasks required, appropriate to the analysis of trace materials, and which meets accepted standards to safeguard the health and safety of staff.

## 5.1 Analytical Space and Facilities

There must be sufficient space to meet workload needs and adequate, conveniently located bench space. Adequate space must be provided to allow staff to perform their tasks with due regard to efficiency, comfort and safety.

### 5.1.1 Safety

Storage space for reagents and samples must meet the relevant safety and health regulations for handling of dangerous materials, including explosion-proof design, and security, etc., as needed.

Special additional precautions must be taken to avoid unnecessary physical, chemical, and biological hazards.

### 5.1.2 Laboratory Environment

The laboratory environment must be conducive to the optimal performance of personnel and equipment, including light, temperature and humidity control. The ventilation system must provide an adequate amount of fresh air, and must be able to remove toxic or noxious fumes.

## 5.2 Suitability for Trace Analysis

Facilities intended for analysis of trace contaminants in the natural environment must be maintained sufficiently clean to ensure accurate and precise analysis at the levels of analyte being encountered, within the specifications of the analytical task.

### 5.2.1 Services

The quality of air, water, electrical, gas, vacuum, and related supplies, etc., must be appropriate to laboratory use, and must be monitored as needed.

### 5.2.2 Reagents

Facilities for the preparation and storage of ultra-pure reagent water and highly purified solvents needed for critical trace analyses must be provided.

### 5.2.3 Cleanup

Appropriate space must be assigned to provide for cleaning, storage, and maintenance of the labwares and sample containers needed for trace analysis.

### 5.2.4 Special

Any special facilities appropriate to the analysis of trace materials as required for a specific analytical services contract must be provided as needed.

### 5.2.5 Clean Areas

There must be adequate separation of 'dirty' and 'clean' areas to avoid contamination of samples or analytical solutions.

## 5.3 Emergency Power

A laboratory emergency power supply may be needed to support essential laboratory services, including sample storage systems, main computer systems, etc.

## 5.4 Computer Backup

A scheduled backup procedure must be provided for computerized data systems and associated software in the event of power failure or system malfunction.

# 6 SAMPLE/WORKLOAD MANAGEMENT

Adequate space must be provided for recording receipt of samples and all related paper work including the recording and reporting of results.

## 6.1 Submission Records

Sample reception records showing date of arrival, tests assigned, sample identification, client, date to be reported by, chain of custody, etc., must be prepared and updated as required.

### 6.1.1 Computerization

Provision for computerized logging of samples and tracking of analytical throughput, and retrieval and archiving of test and quality control results can facilitate accurate transmission and retrieval of information and data.

## 6.2 Sample Acceptability

Samples must be checked for proper preservation, and stored correctly pending analysis. The criteria for sample acceptability, and the action to be taken if they are not acceptable, must be defined, documented and implemented.

### 6.2.1 Sample Deficiencies

Sample deficiencies must be noted for use later when reviewing data quality. The laboratory client should be informed immediately of such deficiencies. Special policies should be established regarding the acceptance and analysis of questionable samples.

Special attention must be given to samples where there are known or suspected health hazards. This could include the use of special labels and storage facilities.

## 6.3 Sample Handling

Samples, and solutions prepared from them, must be stored as appropriate until the required measurements are complete and batch and run quality have been verified.

### 6.3.1 Sample Storage

Proper enclosures must be provided as necessary to ensure the stability of samples until disposal. Such facilities must provide, as appropriate to the specific sample and analytical requirements;

- o climate control (freezer, refrigerator, incubator, etc.)
- o security (locked and controlled storage rooms, etc.)
- o protection from light,
- o proper ventilation, etc.

### 6.3.2 Sample Disposal

Minimum storage times before sample disposal must be established to ensure that the client has an opportunity to review and examine the reported results.

Disposal of samples must be in accord with the relevant regulations, as appropriate to their contents.

## 6.4 Test Assignment

Accurate records must be maintained of samples received, tests requested, analyst or work station to which tests are assigned, work progress, results, and final reports. Sample reception and related records must be dated and initialled by the person responsible.

### 6.4.1 Start of Analysis

Sample holding times must be defined and analyses must be initiated within the time limits required.

## 6.5 Workload Management

The management of samples, test assignments, test initiation and completion, data reporting must ensure that the client's needs are met in a timely fashion. The protocols and procedures whereby this is achieved must be documented. Management reports on workload and throughput will aid in the re-assignment of resources to prevent backlogs.

# 7 ANALYTICAL SYSTEMS

Analytical results must be determined using the analytical test procedures required by the analytical services contract, with due regard to established quality assurance and quality control protocols.

Analytical systems depend on application of a standard procedure for sample preparation, cleanup and analysis, and on the proper operation of laboratory equipment and instrumentation. Systems must be set up and operated to provide or exceed the client's specified data quality and performance requirements. The use of accepted/recognized standard methods is recommended.

## 7.1 Supplies

Reagents, solvents, labwares, and other laboratory supplies must meet the quality requirements essential to trace measurement and analysis.

### 7.1.1 Laboratory Stores

Laboratory supplies must be of proper quality, maintained in adequate quantities, and stored in an appropriate space with due regard for safety, stability, and security.

### 7.1.2 Quality of Supplies

Personnel responsible for stocking supplies, etc. must be kept informed in writing of the special requirements for high quality materials.

Protocols must be documented for checking the quality of supplies. Records of such checks must be kept for review.

### 7.1.3 Disposal

Disposal practices for used and out-dated stocks must be in accordance with the relevant regulations.

## 7.2 Instrumentation and Equipment

General equipment and analytical instrumentation must be provided which is appropriate to the test procedures required under the contract and this code.

### 7.2.1 Safety

No equipment must be operated until it is first shown to be in a safe and reliable state, and then only by personnel who have been thoroughly trained and duly qualified as operators.

### 7.2.2 Capability

All laboratory equipment and analytical instrumentation must be capable of the performance characteristics required to meet contract needs.

### 7.2.3 Stability

Characteristics such as stability, sensitivity, calibration linearity, etc., must be monitored regularly.

### 7.2.4 Maintenance

All laboratory equipment must be checked and calibrated regularly as needed. Records must be kept showing the outcome of both regular scheduled preventive maintenance, and all unscheduled repairs.

# 8 ANALYTICAL METHODS

Analysts must ensure, and demonstrate, that the methods they use will provide the data quality required by the client. Where not otherwise specified, the laboratory must follow currently recognized practices to ensure that its analytical results are of known and appropriate quality.

Methods must specify the factors requiring quality control and the procedures to be followed to forestall the generation of poor quality data.

Method and detection system principles should be summarized together with the expected performance characteristics. These include estimates of the method recovery, repeatability, and the Method Detection Limit, the analytical system sensitivity, and calibration reproducibility.

## 8.1 Definitions

### 8.1.1 Standard Methods

Methods, recognized by professional associations such as AWWA, ASTM, AOAC, etc., which have been subjected to rigorous criteria for method development and verification by inter-laboratory and inter-method comparison, to establish their repeatability, ruggedness, specificity, and recovery, with respect to the measurement of specified sample matrices.

### 8.1.2 Standard Operating Practices

General tasks related to daily laboratory routines which must be documented to ensure proper implementation.

### 8.1.3 Good Laboratory Practices

The ideal toward which laboratories strive, to ensure that their operations will be considered acceptable in the scientific community.

Good technique based on proper education and training, which incorporates appropriate documentation of experimental purpose, tasks, procedures, observations, and conclusions or results.

### 8.1.4 Recovery

The ability of a method to efficiently and consistently extract the target analyte from a certified reference material. Ability to evaluate the recovery efficiency of an analytical method will require an accurately calibrated measurement device.

### 8.1.5 Repeatability

The ability of a method to yield essentially the same result on repeated trials, all performed in a single batch under identical conditions by the same technician.

### 8.1.6 Ruggedness

The ability of a method to withstand reasonable variation in procedure without affecting the repeatability of the test.

### 8.1.7 Sensitivity

The ability of a detection system to observe and measure small changes in response to the analyte levels in a sample.

### 8.1.8 Specificity

The ability of a method to isolate or react only to the targeted analyte. Interferences reflect a lack of method specificity and inability to adequately identify the analyte.

## 8.2 Bench Procedures

Bench procedures must be documented in sufficient detail to ensure proper application. They must be readily available to technical staff, and must be followed as described. When modifications are required because of sample matrix or other factors, they must be noted and appended to the analytical record.

## 8.3 Calibration

Analytical detection and measurement devices must be calibrated and restandardized regularly based on the documented stability of the instrumentation used. The daily standardization should be controlled to forestall between-batch systematic bias.

### 8.3.1 Standards Preparation

All working standards must be of known accuracy, and traceable to internationally accepted reference standards. Preparation procedures must be documented. Materials used to prepare standards must be obtained in the highest purity available and should not be used for other purposes to reduce the risk of inadvertent contamination.

### 8.3.2 Labelling

The concentrations and date of preparation of standards must appear on the label of all standards along with the initials of the person who prepared it and the expiry date.

A tracking system for standards, indicating source of material, name of preparer, date, and other information regarding their use, stability, accuracy, etc. should be maintained.

### 8.3.3 Validation

Cross-checks of old and new standards must be performed and the results recorded. Maximum shelf lives must be established to ensure accuracy is maintained. Comparison against external sources of standards is strongly recommended.

### 8.3.4 Storage and Disposal

Care must be taken in the storage and use of standard solutions to assure their accuracy and to avoid sources of contamination.

Disposal practices for used and out-dated standards must be in accordance with the relevant regulations.

### 8.3.5 Reference Standards and Materials

Laboratories must routinely analyse appropriate reference standards and materials to demonstrate efficient method recovery and analytical accuracy and precision.

### 8.3.6 Reference Standards

Reference standards are essentially single component materials of known physical and chemical properties, specially verified by physical procedures to be of a specified purity. They are used to establish the accuracy of secondary standards and of any solutions prepared from them for the purpose of calibrating analytical detection systems.

### 8.3.7 Reference Materials

Reference materials are natural samples similar in matrix to the real samples to be analysed. They have been thoroughly tested by a variety of methods and laboratories to establish an expected value for one or more sample constituents. They are used to evaluate method and analyst precision and efficiency.

The certified value of a reference material is often stated as falling within a range of values. This range depends on the nature of the material, its homogeneity, the method(s) used to certify it, and the performance of the laboratories that participated in the certification.

Rigorous criteria are applied to ensure the validity of a certified value. Therefore, under controlled conditions, the average of a reasonable number (e.g. n=9) of repeated analyses of a reference material should not differ from the certified value by more than $S_w/\sqrt{n}$. If these criteria are not met, the competent analyst will take other steps to re-affirm the accuracy of in-house standards, and the proper use of the method as compared to the standard method, before deciding that the certified value for the material as received does not apply.

### 8.3.8 Interlaboratory Studies

Laboratories should participate regularly in relevant inter- laboratory performance evaluation studies, to ascertain and verify comparability with peers. Such evaluations should be based on at least two samples (using Youden's two sample technique for detecting systematic error). It is preferable to use at least six samples over the calibrated operating range of most of the participants. This will then permit better evaluation of laboratory precision, slope and blank biases, erratic data, or other analytical difficulties.

## 8.4 Method Performance

Method performance factors must be evaluated regularly. Definitions for the following terms appear in section 9. Method performance is characterized by repeatability, recovery, and specificity. (Accuracy and reproducibility depend on the accuracy of standards and the calibration control procedures.) Note that the validity of the method will depend on the type of sample, the specific constituents that may or may not be present, and their impact on the method and detection system used.

### 8.4.1 Detection Sensitivity

The measurement detection system must be sensitive enough to measure the repeatability of the method. The sensitivity should be adjusted to allow measurement of the variability of the analytical methodology, within the routine operating range required for the samples being analysed.

Reading increments not larger than 0.5 to 1 times the within-batch standard deviation ($S_w$) are needed to obtain valid estimates of repeatability.

### 8.4.2 Analytical Repeatability

Method repeatability must be determined regularly by within-run replication of typical samples, spiked as necessary with known standards to provide a measurable concentration. (See section 3.7.5 on estimating standard deviation $S_w$)

### 8.4.3 Method Detection Limit

The minimum level of replication when determining $S_w$ for the purposes of calculating a Method Detection Limit (MDL) is eight. The MDL must be determined by analysis of typical samples or reagent water, spiked as necessary to provide a concentration which is in the vicinity of the anticipated MDL. It should then be verified by duplicate analysis of routine samples or spiked blanks, accumulated over a significant period of time. (For more details refer to the MOE report "Estimation of Analytical Method Detection Limits")

### 8.4.4 Method Recovery

The method recovery must be verified on a regular basis against certified reference **samples** of an appropriate matrix. The recovery must fall within the accepted limits for the reference material. (Simultaneous verification of calibration accuracy using a reference **standard,** is recommended to ensure proper interpretation of the method recovery check.)

### 8.4.5 Method Quality Control

Laboratories must implement routine quality control (QC) practices, including control charting as necessary, to show the stability of equipment and instrumentation, the purity of essential reagents and solvents, and the overall performance of analytical systems.

# 9 ANALYTICAL CONTROL

Protocols must be established to ensure identification and correction of situations where method or run quality fails to meet specifications. If it becomes necessary to report data for which there are quality problems, the client must be informed of the nature of the problem, and of its possible impact on data interpretation.

Note that the presence of error in a specific result can only be inferred by reference to replicate measurements of the sample and to the relevant quality control data for the method and for the analytical run in which the result was obtained.

## 9.1 Definitions

### 9.1.1 Precision

Ability to limit the spread of replicate measurements relative to their average, in a manner which approximates the bell-shaped normal distribution.

Precision is characterized at three levels:

- the **repeatability** of a method by a single analyst within a single batch of replicate trials within a single laboratory, (excluding the effect of calibration variability);
- the **reproducibility** of a method over a period of time or among a group of analysts within a single laboratory, (primarily a function of the ability to maintain control of the calibration process);
- the **precision** of a method among analysts from different laboratories analysing portions from the same sample, (primarily a function of the comparability of calibration standards and calibration control protocols).

### 9.1.2 Accuracy

A characteristic of the measurement device, achieved by careful, controlled calibration against standards traceable to primary internationally defined reference standards.

Ability to ensure, on the basis of deliberate control activity, that the **average** of repeated measurements of a known reference standard will be acceptably close to the (defined) true value.

It is important to distinguish between the defined accuracy of a primary standard, and the implied accuracy of a calibrated measurement device. Analytical data 'validity' is then a composite of the;

o accuracy of the laboratory's standard,
o accuracy of the calibration procedure and technique,
o repeatability of the method,
o recovery/efficiency of the method,
o degree of control exerted to maintain the above,
o interaction of sample matrix, method, and detection system,
o skill and experience of the analyst.

### 9.1.3 Bias

A systematic difference between two sets of data, or a deviation of an average from an expected value, due to errors or inadequacies in field or laboratory methods/techniques, or by errors in calibration, blank, recovery or other correction factors.

### 9.1.4 Control

Deliberate action, taken to prevent bias, by identifying and reacting to unexpected single results or trends in the average of a sequence of results, based on:

- o definition of an expected value
- o designation of control limits to identify errors
- o an action plan to correct errors

### 9.1.5 Determinate Error

Excessive chronic variability induced by improper technique or operations, such as chronic dust contamination, 'dirty fingers', inadequate sub-sampling, etc.

### 9.1.6 Indeterminate Error

Excessive variability in a data set for which no assignable cause can be determined.

### 9.1.7 Systematic Error

A bias common to a sequence or batch of results, frequently induced by indeterminate or determinate error in a standard, or in the use of a standard.

Examples include use of a contaminated standard, improper correction for a method blank, failure to correct for curvature, inadequate verification of recovery correction factors, or any other factor affecting the correct standardization of an analytical method.

## 9.2 Run and Batch Control

For the purposes of establishing appropriate response to a control problem, the 'batch' operations of sample preparation and cleanup, which affect analytical repeatability and recovery, are distinguished from the 'run' operations of calibration and instrument operation which affect accuracy. Note that several batches can be run together under a single calibration.

### 9.2.1 Batch Processing

Samples should be prepared in 'batches' which include reagent blanks, method blanks, recovery checks, duplicate analyses, etc. This control data may lead to a decision to reject the batch and to re-prepare and analyze the samples involved.

### 9.2.2 Run Processing

Once the detection system has been set up, stabilized, and calibrated, several 'sample batches' may be processed together in one 'run'. The run quality should be assured by use of appropriate calibration control materials, and regular re-analysis of a

reagent blank, low and high standards. These will monitor calibration accuracy, baseline stability, response stability and linearity, and other time-related effects. This data may lead to a decision to re-measure the prepared analytical solutions.

## 9.3 Reproducibility Control

Two types of imprecision can be attributed to:

- o repeatability of a method within a 'batch' of measurements, and,
- o reproducibility of calibration between 'run'.

Under controlled conditions, between-run precision should not be greater than 1.3 to 1.5 times the within-batch variability. Failure to meet this standard suggests inadequate control of accuracy.

## 9.4 Accuracy Control

Two aspects of accuracy can be distinguished based on:

- o the accurate use of accurate standards needed to calibrate the measurement system
- o the efficiency of the analytical method.

Reference materials are generally available to evaluate both components of accuracy. One must affirm the accuracy of in-house standards versus reference standards before attempting to evaluate the recovery/efficiency of the method.

## 9.5 Performance Verification

Management must provide for external and self-audit of the laboratory facilities, equipment, methods, and appropriate operating records to ensure that minimum acceptable practices are being defined and followed.

Ministry officials must be permitted to review the laboratory operation, on a need to know basis, to evaluate implementation of this code as it relates to specific contract or regulatory work.

# 10 DATA REPORTING

Reports of analytical results must include or be accompanied by units of measure, a method code or reference, and any important remarks concerning the sample or analysis which may affect data interpretation. A data quality statement is highly desirable.

## 10.1 Definitions

### 10.1.1 Significant Figures

In measurement, those figures are considered significant which are in the same decimal position, or to the left of, the most significant digit of the calculated analytical standard deviation. Leftmost zeros are used only to locate the decimal place. The result 0.00001234500 appears to have 7 significant digits, since the rightmost zeros are considered significant.

| | |
|---|---|
| e.g. if the standard deviation is | 0.0023 |
| and the measured result is | 1.230456 |
| the indicated digits are significant | ^.^^^ |

### 10.1.2 Reporting Increment

The interval between successive reported values, introduced by rounding or truncation of non-significant figures. This interval should be smaller than the measured analytical standard deviation.

e.g. if the standard deviation is 0.0023
results are reported to at least the nearest 0.002

### 10.1.3 Reporting Limit

The point below which measurements are not reported. Typical alternatives for a reporting limit include:

- o the reading/reporting increment (RI)
- o the instrument detection limit (IDL)
- o the method detection limit (MDL)
- o the limit of quantitation (LOQ)
- o the practical quantitation limit. (PQL)

The definitions for these terms are relatively arbitrary depending on the various professional or government agencies which use them. They are often purported to provide a certain level of statistical or professional confidence in the probability of analyte being present in the sample.

### 10.1.4 Low Level Qualification Limit

The point above which the professional analyst has confidence in both the qualitative and quantitative validity of the result. In other words, the analyte causing the response has been adequately characterized and identified, and the amount reported is free of significant bias.

### 10.1.5 Detection Limit

A criterion used to assess the presence of analyte in a sample, based on the assumption that the analyte is not present. It is a statistically defined point above which there is less than a specified risk of 'type I' and 'type II' decision error. It is determined as a factor times the known repeatability of measurement under standard conditions. It does not incorporate an allowance for bias, misidentification, under-recovery, or sources of sample matrtix effects.

Type I Error: a decision that analyte is present in the sample, when it is not present.
(i.e. false positive decision error)

Type II Error: a decision that analyte is not present, when in fact it is present.
(i.e. false negative decision error)

## 10.2 Round-off

Data must not be rounded off in excess of the established repeatability of analysis as estimated by the standard deviation obtained by replicate analysis of typical samples or spiked blank samples, performed within the same analytical batch. A third significant digit may be dropped or rounded-off if the client indicates no need for three significant digits. However, in order to avoid a reporting increment of greater than 5% of the reported value, the third figure should not be rounded off or truncated when the leftmost significant figure is a 1.

e.g. assuming that the standard deviation is about 0.0002, one should normally report in increments of about 0.0002 , however

given 0.0234 one may truncate to 0.023
i.e. report to nearest 0.001)
(an increment of 0.001 is < 5% of 0.023)

given 0.0136 one should report to the nearest 0.005 at least
(not round to 0.014 or truncate to 0.013)

## 10.3 Verification

Data must be verified using available cross-checks, such as upstream vs downstream results, ion-balance, total greater than dissolved, parameter ratios, etc., within the tolerances of analytical precision.

## 10.4 Data Quality

The overall quality of analytical data must be evaluated in terms of sample matrix effects, methodological effects, and measurement system (e.g. instrumental) effects. The basis for evaluation should include knowledge of method recovery, sample matrix interferences, analytical repeatability, method detection limits, calibration reproducibility and accuracy, and other sources of bias.

Problems which might impact on instrumental (run) or method (batch) data quality must be evaluated and corrected, where possible, before analyzing samples.

## 10.5 Data Interpretation

Four statements can be made about an analytical measured result (MR), assuming the absence of bias or other error. The preset criterion is set at a statistically determined factor times the analytical standard deviation.

a) analyte is present in a range centered on MR,

b) analyte is present in the sample at a level > zero, with a specified risk of analyte being absent (e.g. <14%)

c) analyte is not present in the sample at a level exceeding MR + a preset value

d) analyte is not present in the sample at a level below MR - a preset value

These statements are based on the known repeatability of the analytical method. The risk of the statement being incorrect can be determined from statistical tables. For the purposes of the example we will assume that the limits for cases b), c), d) is 3 times $S_w$. In case a) the probable range is plus or minus 2 times $S_w$.

Example: A measured result of 0.123 is obtained for a test with a standard deviation of 0.057 based on a large number of replicate measurements. $3\ S_w = 0.171$, $2\ S_w = 0.114$.

We can conclude:

a) The sample does contain an amount between 0.000 and 0.237 (risk of error is <5%)

b) There is a risk of <15% that a result of 0.123 could be obtained from a sample which does not contain the analyte.

c) There is very little risk that the sample contains more than 0.294

d) The risk of a sample containing analyte at a level below the criterion MR - 3 $S_w$ would not be assessed until the measured result is > $3S_w$.

Note: In case b) the Detection Limit (DL) is normally set to ensure a false positive decision risk of <1%. When a result is below the DL, we cannot conclude with certainty that the analyte is present. If we do so, there is a possibility of a false positive decision. However, in this instance the risk of a false positive is less than about 15%. The suspicion that analyte is present is supported by the range given in case a). Failure to report this measurement may cause the data user to conclude incorrectly that the analyte is absent (i.e. a false negative decision error).

Note: If we wish to put an upper or a lower limit on the possible content of a sample we should use case c) or d) respectively.

## 10.6 Low-level Data Reporting

The client's specific data reporting requirements must be determined in advance. The two alternatives are:

a) to report results ONLY when they fall above a predetermined level, generally set at a factor times the standard deviation of the method. These reporting limit options may be based on:

statistical principles;
- MDL (Method Detection Limit) = 3 S
- LOQ (Limit of Quantitation) = 2 MDL
- PQL (Practical Quant'n Limit) = 5 MDL

or on data use criteria;
- not lower than (e.g. 1/10th) of the health or other relevant water quality standard, etc.

b) to define a reporting limit (W) in the range 0.5S to S and to report ALL results equal to or greater than W, but to qualify results as 'tentative' or 'trace' using a code such as <T when they are below a predetermined level T set at some factor (e.g. 5 or 10) times W.

## 10.6.1 Option a: Withhold (e.g. <DL coded)

The MDL is the point above which there is < 1% risk of falsely concluding that the analyte is present at a non-zero level. The actual factor depends on the amount of data used to calculate S.
It is based on purely statistical principles.

The LOQ (one perspective) is the minimum level that must be in the sample to ensure that a result lower than MDL will not be observed (risk of <1%), based on purely statistical principles.

The PQL is an arbitrary level chosen on the premise that errors due to bias or mis-identification will be negligible above this level. In as much as many analytical calibration ranges do not extend beyond 50 to 100 times S, the PQL represents a result greater than about 20 to 30% of the calibrated range.

The choice of one of these alternatives is relevant when there are measurable amounts present in the samples of interest, and there is no need to report 'trace' level measurement data. It is usually recommended based on the need to avoid 'false positive' action (i.e. to avoid taking unnecessary action).

This option can lead to a high risk of 'false negative' decisions, (i.e. failure to take necessary action) when the levels generally encountered are at or below the chosen reporting limit.

## 10.6.2 Option b: Report (<W, <T coded)

In as much as analytical results are 'digitized' on the basis of a reading increment RI, which should be not greater than the analytical standard deviation, any result which is less than one increment from zero represents a 'zero' measurement. The reporting limit W can be set equal to RI.

Results below W are deemed to be 'zero results' and are reported as the value of W qualified by the code <W.

Results equal to or greater than W, but below some higher value (T) are considered to be 'trace results'. Option a) does not report traces. Option b) does report the measured trace value. But such results are qualified as being unreliable by use of a remark code such as <T.

The following is a discussion of the rationale for this practice. Also refer back to section 10.5.

The risk that a result greater than a specified factor times $S_w$ will be obtained from a sample containing none of the analyte can be determined from the statistical *t*-table. Alternative values for the factor 't' are given in the following table along with the risk of a poor decision.

| **RISK of false positive** | **t-factor if $S_w$ based on 8 replicate** | **t-factor if $S_w$ based on >40 replicate** |
|---|---|---|
| <40 % | .26 | <.26 |
| <30 % | .55 | <.53 |
| <20 % | .90 | <.85 |
| < 5 % | 1.9 | <1.7 |
| < 1% | 3.0 | <2.4 |

Any result greater than about 0.25 S suggests the presence of an analyte in the sample with a risk of error of <40%. Results greater than 0.9 S should occur less than 20% of the time if the sample contains none of the analyte.

When the samples are expected to contain 'trace' levels, failure to report traces (as opposed to 'zeros') can forestall the detection of potentially hazardous contaminants in the environment. Provided sufficient data is gathered, the distinction between a 'zero result' and a 'trace result' achieved by use of this option, may permit trend analysis or preliminary isolation of parameters of concern.

## 10.7 Remark Codes

Analytical results should be qualified to reflect problems related to sample matrix, interference, potential under or over recovery.

# 11 RECORDS AND DATA MANAGEMENT

Analytical results must be recorded and archived along with the information required to ensure traceability to all associated procedural, quality control and performance evaluation records. An acrchiving policy must be established to ensure secure retention of analytical and QA/QC records until destruction is authorized by the laboratory client.

## 11.1 Operational Documentation

All procedures and operating practices associated with the processing and tracking of samples, the collection and reporting of quality control information, and the collection and reporting of analytical test results, must be documented.

### 11.1.1 Documentation Approval

There shall be a protocol for approving new documentation and for removing old or obsolete documentation from service.

## 11.2 Data Management

The procedures employed for collection and archiving of analytical results, and associated data management must be documented. These will include:

- verification
- reporting
- retention
- security

Typical analytical records include:

- equipment and instrument maintenance logs;
- analytical run records;
- laboratory work books;
- instrument printouts, charts, etc.;
- quality control data;
- quality assessments;
- final reports;
- sample reception records;
- chain of custody records;
- other related documentation.

### 11.2.1 Analytical Records

Operational log-books showing tests assigned, the analyst responsible, and related information needed to process samples, must be maintained.

Analytical workbooks must record the date and time analysis started, the analysts participating, the analytical run(s) within which analysis and measurement was performed, and all related quality control observations.

### 11.2.2 Quality Control Records

Laboratories must maintain all records necessary to show that the analytical systems used were in control at the time services were provided. The results of these quality

control and performance monitoring checks should be separately tabulated and summarized for ready retrieval, evaluation, and audit. They must be retained for review by the laboratory client.

### 11.2.3 Record Security

Records should be stored in a manner that ensures their security and physical protection. A retention time should be established for each type of record.

### 11.2.4 Record Corrections

A protocol for correcting data or records or reports must be established. Corrections to data should be made in such a manner that the original data is legible.

### 11.2.5 Data Base Corrections

A protocol must be established for timely correction of information or data in computerized data systems. This protocol must ensure data base security and must provide for an audit trail of any corrections or changes made to the data base.

## 11.3 Record Review and Approval

Analytical reports and associated records should be reviewed and authorized before they are released to the client. Records relating to data quality should be available on request for client evaluation and review.

## 12 READING LIST

The analytical and quality control literature provides innumerable references on the planning and management of quality in the environmental laboratory setting. The text "The Chemical Analysis of Water" by D.T.E. Hunt and A.L.Wilson, includes a number of lists of references to relevant papers.

Certain authors, in particular, W.J. Youden, A.L. Wilson, and J.K. Taylor are invaluable. A number of associations and institutions such as AOAC, ASTM, ISO, US-EPA and NBS, CSA, provide guidelines regarding the type of documentation expected in order to be prepared for a laboratory inspection or accreditation. The following indicates some of the books and papers available.

### 12.1 General Literature:


| | |
|---|---|
| Keith, L.H. Et Al | "Principles of Environmental Analysis"; ACS Committee on Environmental Improvement, Anal.Chem., 1983, 55, p2210-2218 |
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## 12.2 Texts:

APHA: American Public Health Association
1015 18th Street, N.W., Washington, DC 20036, USA

Quality Assurance Practices for Health Laboratories
Inhorn, Stanley, L. (Editor)

AOAC: Association of Official Analytical Chemists
1111 N. 19th Street, Suite 210-P,
Arlington, VA 22209 USA

Quality Assurance Principles for Analytical Laboratories
Garfield, F.M.

Statistical Manual of the AOAC
Youden, W.J. and Steiner,E.H.

ASTM: American Society for Testing and Materials
1916 Race Street, Philadelphia, PA 19103, USA

Evaluation and Accreditation of Inspection and Test Activities STP 814
Schock, Harvey, (Editor)

Quality Assurance for Environmental Measurements STP 867
Taylor, J.J. And Stanley, T.W. (Editors)

ACS: American Chemical Society
1155 16th Street., N.W., Washington, DC 20036, USA

Detection in Analytical Chemistry,
ACS Symposium Series No. 361
Currie, Lloyd A. (editor)

CSA: Canadian Standards Association
178 Rexdale Blvd., Rexdale, Ontario, M9W 1R3

Quality Assurance Standards CAN3-Z299

SCC: Standards Council of Canada
350 Sparks Street, Ottawa, Ontario, K1R 7S8

Guidelines for Preparing an Application for Accreditation CAN-P-1501B (referring to CAN-P-4)

RSC: Royal Society of Chemistry
Burlington House, London W1V 0BN

The Chemical Analysis of Water
General Principles and Techniques
Hunt, D.T.E. and Wilson, A.L.

OMOE: Ontario Ministry of the Environment
Laboratory Services Branch, QA Office,
PO. Box 213, Rexdale, Ontario, M9W-5L1

Credibility: The Consequence of Quality Assurance
Quality Management Plan
QA Policies and Guidelines
Principles of Control Charting

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